The Law of Multiple Proportions

Background

The beginning of the wide acceptance of a modern atomic view of chemical change is generally traced back to the early 1800's and John Dalton's various publications which alternately philosophized, cajoled and demonstrated with simple (and somewhat inaccurate) data that the concept of indivisible particles which gave each kind of matter its unique characteristics was all but obvious.

The prior work of Lavoisier (who demonstrated conservation of mass during chemical change) and Proust (who formulated the *law of definite composition*) served as the perfect backdrop for Dalton's theorization which had an unlikely beginning with his keen interest in the weather and eventually culminated in a statement of partial pressure behavior among gases (correct but based on false ideas) and the law of multiple proportions with which he sought to further cement the idea of constant mass among identical atoms and advance his own ideas about how atoms might combine to form compounds.

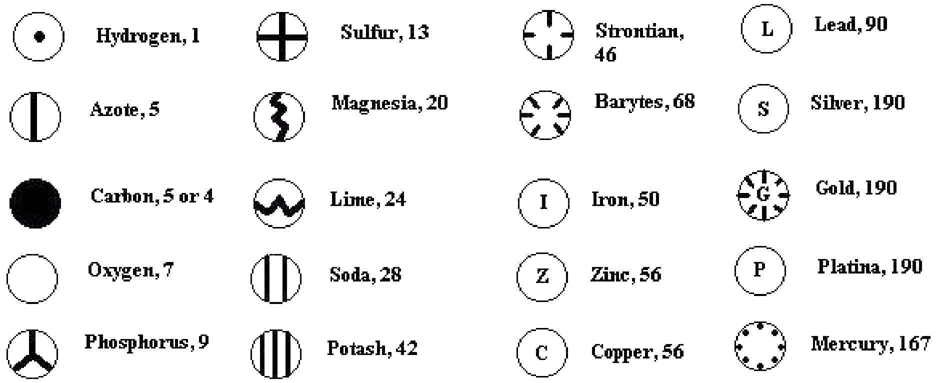
If Dalton's experimental skills were somewhat weak, his intellect was certainly not in question--at least not to the locals of Manchester who hired him to teach school at the age of twelve! (Dalton was forced to leave school as a student the year before in order to seek gainful employment). He kept very careful daily records of the weather (a pastime which Jacob Bronowski described as a "singularly monotonous task" considering the Manchester climate) and was led to wonder by his observations about the nature of gases (which he called *elastic fluids*) and phase changes. He eventually concluded that when water evaporated it changed from the liquid state to a gas which mixed with the gases already known to be present in the air (principally nitrogen--which he called *azote*--and oxygen). The mixing of gases intrigued Dalton and got him to thinking about forces of attraction and repulsion which might either enable or prevent mixing of gases. He thought that atoms of the same element might repel each other but attract different atoms and so that would result in spaces between similar atoms into which others might fit. In his view this would prevent the "settling out" of heavier gases and make each gas contribute to part of the total pressure in proportion to its quantity. Clearly heavy gases did not settle out of mixtures and simple experiment confirmed his suspicions regarding partial pressure.

Dalton's attempt at sorting out how elements combine to form compounds was grounded in his simple ideas about repulsive and attractive forces among atoms and Proust's data supporting the law of definite composition. Dalton's major (and stubbornly held) error was in interpreting the data. He insisted that the simplest compound of two elements would be binary, e.g., water would be HO. There might be other combinations (he was aware of several different oxides of nitrogen) but there would always be a 1:1 combination.

Since hydrogen was the lightest known element it made sense to Dalton to assign it a relative mass of 1. Proust had shown that in water the mass ratio of hydrogen to oxygen was always 1:8. Therefore, oxygen had a relative mass of 8 [actually, the data were not that good and 7 was the value Dalton chose for oxygen; coupled with his erroneous assumptions about the nature of simple compounds, this resulted in a seriously faulty relative mass scale]. Proceeding on similar assumptions, Dalton created a table of relative masses for known elements.

Adapted from Chemical Principles in the Laboratory, 4th ed., Emil J. Slowinski, Wayne C. Wolsey, William L. Masterton

Dalton's Table of Elements, 1803



Dalton further hypothesized--based on known compounds--that it was possible for elements to form different compounds if their atoms were attracted to one another in different proportions. He used as evidence for this hypothesis substances like carbon monoxide and carbon dioxide, as well as the various oxides of nitrogen such as NO, NO_2 and N_2O. But keeping to his fundamental idea that atoms were indivisible and only rearrangement of atoms was involved in chemical change, he insisted on integer mass ratios relating the variable element in such compounds.

The case of CO and CO_2 is particularly simple for illustrating the *law of multiple proportions*. The element of "constant mass" is carbon (taking today's relative mass, 12). The mass of oxygen in the two compounds varies. It is 16 in carbon monoxide and 32 in carbon dioxide. These two values are in a simple whole number ratio, i.e., 16:32 = 1:2.

The law can be applied to slightly more complicated cases with just a little more work. For example, N_2O_3 and NO are not as obviously related. If we select nitrogen as the "constant mass" in this pair of compounds, we will have to take two NO to compare with one N_2O_3:

Compound	mass of nitrogen	mass of oxygen
N_2O_3	28	48
2 NO	28	32

The masses of the variable element (oxygen) are in a 48:32 ratio. This is 3:2.

Illustrating the Law of Multiple Proportions in a laboratory exercise presents no special challenge. One of a number of fairly common compounds can be used with good results. In particular, copper(II) bromide makes an excellent choice for a variety of reasons. The chemistry behind its eventual decomposition into elements is both visually and theoretically interesting and fairly easy to coax into convenient "steps" along the way from $CuBr_2$ to CuBr and then finally to Cu.

The bond between copper and bromine in the compound is not especially strong. The electronegativity difference between the two elements is only 0.9, indicating a significant degree of covalent character. The bond is weak enough that the heat from a Bunsen burner is sufficient to initiate partial decomposition:

$$CuBr_2(s) \rightarrow CuBr(s) + Br_2(g) \qquad \text{[not balanced]}$$

A close look at this reaction reveals that the bromine is an oxidation product and the copper in the compound has been reduced.

Copper(I) bromide can be further decomposed by heat but only with difficulty using a Bunsen burner. Instead, an excess of nitric acid is used to decompose the compound into bromine and aqueous copper(II) ions:

$$CuBr(s) + NO_3^-(aq) + H^+(aq) \rightarrow Cu^{2+}(aq) + Br_2(g) + NO(g) + H_2O(\ell) \quad \text{[not balanced]}$$

In contact with oxygen from the air NO becomes NO_2. The bromine can be driven off by heating.

Continued heat removes the water from the system and the residual solid copper(II) nitrate will begin to decompose:

$$Cu(NO_3)_2(aq) \rightarrow CuO(s) + NO_2(g) + O_2(g) \quad \text{[not balanced]}$$

Because the amount of copper in the experiment theoretically remains constant, it is possible to use the mass data for each compound to illustrate the law of multiple proportions <u>if that constant mass of copper can be determined</u>.

The reduction of CuO to copper metal can be accomplished in a variety of ways. Historically this kind of process has been done by heating the metal oxide in a reducing atmosphere of hydrogen or even methane. Both of these gases form explosive mixtures with oxygen or air and therefore there are reasons not to employ such methods if good alternatives are available.

If the copper oxide is dissolved in dilute acid, copper(II) ions become available in solution. The addition of a more active metal such as zinc will then initiate a quantitative displacement of copper metal which can be recovered and compared to the masses of each compound in the step-by-step conversion process. If a slight excess of acid is used, any leftover zinc metal will displace hydrogen from the mixture and go into solution and is easily separated from the solid copper product.

The Experiment

There are three parts to this experiment:

- the conversion of copper(II) bromide to copper(I) bromide
- the conversion of copper(I) bromide to copper(II) oxide
- the reduction of copper(II) oxide to copper metal

The following non-locker materials will be provided:

- glass tubing and tubing cutters
- 18 x 150 test tube with 1-hole stopper
- utility clamp with plain metal jaws
- 500 mL Florence flask
- approx. 0.1 M NaOH
- 16 M HNO_3 [fume hood]
- 6 M HCl
- granular zinc

The Chemicals

Copper(II) bromide is an almost black, iodine-like solid in either fine, deliquescent crystals or powder form. It is very soluble in water and melts at 498°C. It is used in photographic work, organic synthesis (as a brominating agent), as a wood preservative and in some solid-electrolyte batteries.

Bromine is a dark reddish-brown fuming liquid at room temperature, consisting of diatomic molecules. In dilute water and hexane solutions its color varies from golden to dark orange. In basic solutions at room temperature it slowly reacts to form bromide and hypobromous ions. It is a member of the halogen family and has a chemistry similar to chlorine. It attacks all metals and organic tissues and vaporizes readily at room temperature. Fumes are highly irritating to eyes and lungs.

Bromine is used for bleaching silk, disinfecting spas, and manufacturing anti-knock compounds. Pure liquid bromine on the skin can cause painful, serious burns which heal only slowly.

Nitric acid has been called "aqua fortis" (strong water). It is generally produced by the oxidation of ammonia followed by reaction of the gaseous products with water. When pure it is a colorless liquid that fumes in air with a characteristic choking odor. "Concentrated" nitric acid is a water solution containing 70% HNO_3 (16 M). Even dilute solutions will stain woolen fabrics and animal tissue yellow. It is a very strong oxidizing agent, reacting violently with most organic matter.

Nitric acid is used in the manufacture of fertilizers, dye intermediates and explosives.

Nitrogen oxides produced in this experiment include *nitrogen monoxide* (NO) and *nitrogen dioxide* (NO_2), collectively known as NO_x. The former is a colorless gas which is deep blue as a liquid. It is used in large quantities in the manufacture of nitric acid. When in contact with air NO immediately reacts to form NO_2. This second gas is reddish-brown and is an equilibrium mixture of the colorless dimer, N_2O_4, and the colored NO_2. The gas decomposes in water to form nitric acid and NO and reacts with alkalis to form nitrites and nitrates. It is used in the manufacture of both nitric and sulfuric acids and has been proposed as an oxidizing liquid in rocket propulsion.

Nitrogen dioxide is extremely toxic. As little as 200 ppm can be fatal. Oxides of nitrogen are produced as by-products in internal combustion engines and contribute to air pollution and acid rain. They can also catalyze the decomposition of ozone in the upper atmosphere.

Sodium hydroxide is commonly known as lye or caustic soda. It is a very hygroscopic white solid (absorbs water from the air rapidly) and also absorbs CO_2. It is very corrosive to vegetable and animal matter and aluminum metal, especially in the presence of moisture. Dissolving NaOH in water generates considerable heat.

Besides its use in the laboratory, sodium hydroxide is used in commercial drain cleaner preparations, to treat cellulose in the manufacture of rayon and cellophane and in the manufacture of some soaps. It is corrosive to all tissues and can be detected on skin by the "slimy" feeling associated with bases. It should be rinsed off thoroughly upon contact. It can damage delicate eye tissues and cause blindness.

Hydrochloric acid is also known as muriatic acid. It is the same liquid acid that is often used in controlling the pH of swimming pool water. It is sometimes colored yellow by iron impurities, traces of chlorine and organic matter. Reagent grade HCl contains about 38% hydrogen chloride gas, close to the limit of its solubility at room temperature.

Hydrochloric acid in concentrated form (12 M) has the sharp, choking odor of hydrogen chloride. It is used in the production of other chlorides and in refining some ores (tin and tantalum), cleaning metal products, removing scale from boilers and heat-exchange equipment, and as an important laboratory reagent (often in diluted form).

Concentrated solutions cause severe burns; permanent visual damage may occur. Inhalation causes coughing, choking; inflammation and ulceration of the respiratory tract may occur. Ingestion can be fatal.

Zinc metal is generally obtained from ores of zinc containing sulfur. Its abundance in the earth's crust is about 0.02%. Zinc is a fairly reactive metal which combines readily with oxygen, sulfur and the halogens. Pure zinc, when exposed to air gradually becomes coated with white zinc carbonate ($ZnCO_3$). Most zinc compounds are colorless in solution (or white as solids). Zinc is readily attacked by dilute acids, releasing hydrogen as it dissolves. It is used in corrosion protection (*galvanizing*) and its compounds are employed as paint pigments and disinfectants.

Copper makes up about 0.01% of the earth's crust. It is one of the earliest known metals and is known for its unique reddish color when pure. However it becomes dull when exposed to air, forming oxides of copper, and in moist air becomes coated with green copper carbonate (this is part of the patina that appears on old copper or copper alloy exposed to the elements--like the Statue of Liberty). It is very slowly attacked by dilute hydrochloric acid and sulfuric acid, while nitric acid can readily dissolve it. It also slowly dissolves in aqueous ammonia.

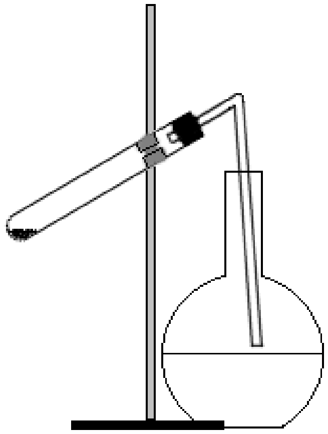
Copper is used in the manufacture of bronzes (copper + tin) and brasses (copper + zinc), and is used extensively in electrical conductors (wires, printed circuits, etc.). Of course copper also makes up a percentage of nearly all U.S. coins minted today.

Copper itself probably has little or no toxicity, but some of its compounds can be quite hazardous.

Technique Discussion

In an experiment of this type the most important consideration--after safe technique--is judicious sample handling to avoid loss. Careful use of the analytical balance and thorough inspection of the sample each time before making a measurement will pay off in more accurate results. Cooling the test tube to "finger comfort" is essential before massing *each and every time*.

About 1 gram of copper(II) bromide should be used. The compound can be heated safely in a test tube, the bromine and other noxious materials safely diverted through a bent glass delivery tube into a reservoir of dilute sodium hydroxide. The base slowly reacts with the bromine as well as any nitrogen oxides released in later parts of the decomposition. *Whenever a heated system exhausts through a delivery tube into a container of liquid care must be exercised to prevent backflow if the temperature should drop in the system.* The typical result is a steam explosion as cool liquid contacts the hot walls of the system. Needless to say, such an eventuality does not improve chances for good results--or survival. The end of the delivery tube should therefore be close to the surface of the liquid BUT NOT TOUCHING IT.



When heating a solid for decomposition as in this experiment, tilting the test tube at an angle and distributing the solid in a thinner layer will speed up the process. Since bromine gas and nitrogen dioxide gas are both heavier than air, some "driving out" of the gases will be needed, playing the burner flame along the test tube length, slowly moving from the bottom to the top, but carefully avoiding the area where the stopper is inserted. Charred rubber clinging to the top of the test tube will contribute to poor results.

In many cases, due to the small diameter of the delivery tube, it is nearly impossible to expel all of the noxious fumes from the test tube. At some point determined jointly by the student and instructor the test tube (still stoppered) may be moved to the fume hood where the delivery tube can be gingerly removed and the test tube heated open until all bromine or nitrogen dioxide gas has been expelled. Bromine has a tendency to condense at the terminal end of the delivery tube and before carrying a test tube through the lab you should inspect your setup to determine if it is safe to move.

Once the initial decomposition is complete, approximately 2 mL of concentrated nitric acid should be added [in the fume hood] and the delivery tube replaced in the test tube before returning to the workstation. Because the reaction often commences without heating it is important that everything be ready to go. It is a good idea to have the test tube already in the clamp with the angle adjusted properly so that it is only necessary to slide the clamp onto the ring stand. BE SURE the swivel on the clamp is tightened securely. Tipping the test tube at this point is likely to result in loss of sample since the contents will be liquid.

Heating a small amount of liquid in a test tube demands more care than heating a solid. Playing the burner flame cautiously over the liquid near the shallow leading edge will help to prevent a sudden bumping which could spurt some sample into the delivery tube. The object is to remove as much water as possible before heating the sample strongly to complete the decomposition. During this process vaporizing/condensing acid *should* dissolve any solid residue on the sides of the test tube. Complete venting of residual bromine/nitrogen dioxide may require a second trip to the fume hood once the sample has been heated to dryness.

The final step in the conversion to copper metal requires dissolution of the oxide. For this process the test tube can be clamped vertical and about 5 mL of 6 M HCl added. The oxide should dissolve readily but gentle heating may help. Again, heating solutions in test tubes is tricky. *If the sample spurts out because it is heated too rapidly the entire experiment is ruined.* After dissolution is complete an equal volume of distilled water can be added.

Based on the starting mass of copper(II) bromide, about 0.5 g of zinc should provide an adequate excess to displace the aqueous copper ions from solution. Because the solution is about 3 M HCl it will react vigorously with the zinc to produce hydrogen gas bubbles and adding the granules too rapidly or all at once will probably result in sample loss. As the copper forms it has a tendency to aggregate into a single spongy ball which can trap unreacted zinc inside it. Periodic division of the ball with a stirring rod or rubber policeman can help prevent this but care should be exercised not to subdivide the sample too much. When all of the zinc has eventually been added the sample can be warmed gently to speed up the reaction of excess zinc. Boiling the sample vigorously is a mistake. It increases the risk that the newly formed copper will be ejected from the test tube and/or will be broken down into fine particles which cannot be recovered.

Recovery of the solid copper mass involves carefully decanting the liquid, adding about 10 mL of diluted HCl (10-fold), heating gently, and then decanting that wash. At least 4 additional washes with distilled water should follow. Failure to completely wash the spongy sample will result in retention of zinc chloride and inaccurate mass data. Over zealous manipulation of the sample will result in its breakup and consequent loss during decanting.

The washed copper sample (still in its test tube) can be placed in a 100 mL beaker with your locker number on it and dried in the oven overnight before final massing.

The Report

Your initial calculations should include:

1. The mass of copper(II) bromide used

2. The stoichiometric masses of copper(I) bromide, copper(II) oxide and copper metal expected

3. The mass of copper(I) bromide [relative error based on stoichiometric prediction]

4. The mass of copper(II) oxide [relative error based on stoichiometric prediction]

5. The mass of metallic copper [relative error based on stoichiometric prediction]

6. The mass of bromine present in copper(II) and copper(I) bromide.
   [relative error in Br masses based on stoichiometric prediction]

7. The mass of oxygen present in copper(II) oxide.
   [relative error in oxygen mass based on stoichiometric prediction]

8. The empirical formulas of all three compounds based on the data.

Your conclusion to this experiment should include a demonstration, using your data, of the law of multiple proportions. If your data does not illustrate the law, you should explain why, using appropriate error analysis. In addition, you should give literature references which support your formulas for the three compounds (color, for example). You should also give the balanced equations for each step in the conversion of copper(II) bromide to metallic copper.